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Recent Developments in Health and Environmental Applications of Micro and Nanostructured Conducting Polymers

Shelley Claridge*

Department of Chemistry, Purdue University, West Lafayette, Indiana, USA

Introduction

Conducting polymers are, without question, outstanding materials. Their unique combination between metal-like, electrical, magnetic and optical properties and the process ability of polymeric materials consolidated their use in the electrochemical sciences over the past decades. However, the versatile character of these polymers combined with the advent of nanoscience has expanded their horizon of applications, now entering the fields of biomedicine and life science, as well as the environmental sciences. This review brings the latest advances on the use of conducting polymers micro and nanostructures in biomedical applications, such as controlled drug release, artificial muscles and tissue engineering, where their stimuli responsiveness has shown new and exciting possibilities. Moreover, this review shows that the use of conducting polymers in effective extraction and pre-concentration of trace amount pollutants from complex matrices resulted in extraction capacities often superior to the materials currently commercialized. More than extracting contaminants, conducting polymers have shown further promising results in the degradation of organic contaminants through photoelectrocatalysis. New features in the synthesis of these polymers are also addressed.

Description

Ever since their discovery, conducting polymers (CPs) found their way to the very heart of electrochemical science and therefore gained a huge amount of applications. More recently with the advent of nanoscience, conducting polymer nanostructures such as nanoparticles, nanowires, nanotubes, nanofibers and many others once again captured the attention of researchers due to their increased surface area, surface roughness and surface area to volume ratio, which results in increased electrical conductivity and electrochemical activity, higher carrier mobility and special optical properties, which widened even further the fields of application of this class of polymers. Nowadays, more than a material for energy storage devices, conducting polymers found their way to the widest range of applications, including many uses in environmental and health applications, which is the focus of this review.

The nanoscale itself has gained space in medical areas, resulting in the advent of nanomedicine an interdisciplinary field that involves the use of nanoscale materials in the life sciences. Within this scenario, conducting polymers have shown good results regarding biocompatibility, especially polypyrrole and PEDOT and with the contribution of the nanoscale, a larger use of CPs for biomedical and health applications is happening nowadays, spreading from drug delivery to artificial muscles, also including the construction of implants and prosthetics, cancer treatment and tissue engineering. The medical interest in intrinsically conducting polymers arises from the existence of electrically active or electrically responsive tissues in our organism, such as skeletal muscles, our heart and of course our brain and the possibility to use the electrical properties of CPs to expand treatments and diagnosis tools regarding these electrically responsive parts of our living organism.

In addition to new challenges in the life sciences, the world's large population growth has consequently led to a greater use of water resources in the last century, which brought up a discussion about water quality, whether for consumption or not. In recent years, studies have reported the presence of pollutants in very low concentrations in the aquatic environment, where the vast majority of these contaminants are found in trace level. The demand for analytical methods that can allow precise determinations of these compounds in the environment has grown dramatically in the recent years, mainly due to adverse effects that these contaminants can cause on human health and aquatic ecosystems. Moreover, these pollutants are dispersed in complex matrices (high number of compounds from different classes) with an elevated degree of sample-to-sample variability [1-3].Therefore, continuous search for sensitive and selective analytical methods capable of identifying and quantifying organic compounds in trace levels has stimulated the development of research in sample preparation, in order to obtain methods with less solvent consumption, high selectivity, fast, with high level of automation and low cost.

Sample preparation is a crucial step before quantitative analysis, aiming the preconcentration of analytes and the remotion of interferes, since the accuracy and precision are highly dependent on adequate sample treatment. Several sample preparation methods based on solid phase materials have been developed and applied for pollutant adsorption in aqueous matrices. In this scenario, the use of ICPs as new adsorbent materials has presented itself as a great alternative, mainly due to ICPs properties as hydrophobicity, acid–base character, π–π interaction, polar functional groups, ion exchange properties and electro activity. More than sample preparation and selective determination of pollutants concentration, the degradation of these substances itself is of great importance. To do so, advanced oxidation processes (AOPs), are a great alternative to remove organic materials from wastewater via oxidation with strong oxidants such as hydroxy radicals. Among the AOPs, heterogeneous photo catalysis (PC) has gained space, mainly with the use of TiO2-based photo catalysts. However, this material has several drawbacks and aiming the efficiency improvement of this material, came the development of photo electrochemical processes (PEC), which are based on the use of photoactive coatings onto conducting materials. In general, the presence of conducting polymers in PEC electrodes can overcome many of the current disadvantages. The possibility to work with different conductive polymers and semiconductors enhances the applicability of PEC in the most different areas, ranging from pollutant degradation to CO2 conversion. However, this is an area in ascension and has a wide application; in this context, the preparation of nanostructured materials may improve even more the PEC capability due to the increased surface area. As widely known, conducting polymers can be synthesized by different methods, such as chemical, electrochemical, photochemical, emulsion and plasma polymerization and radiolysis and the synthesis conditions have great impact in the CP properties. The two most traditional syntheses are undoubtedly the chemical and electrochemical routes. However, due to the expansion in the realm of applications of CPs new routes to form them were developed, as discussed below [4].

Micro or nanostructures of conducting polymers can be synthesized in aqueous medium either by chemical or electrochemical polymerization using different strategies, as soft or hard template assisted method, template-

***Address for Correspondence:** Shelley Claridge, Department of Chemistry, Purdue University, West Lafayette, Indiana, USA, E-mail: sclaridg@purdue.edu*

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free method, electro spinning and ultrasound assisted synthesis. The hard-template methodologies usually employ solid materials, as aggregates or membranes, that guide the formation of the conducting polymer in the shape of the micro or nanostructure of interest. The hard template can be removed after the synthesis or can be present as a composite in the final material. The soft template methodologies use soft materials to synthesize the micro/nanostructured conducting polymer, as surfactants, liquid crystals, organic acids, among others. Surfactants are extensively used in the soft template synthesis because they can form micelles after the critical micelle concentration (cmc).

The micelles can confine the monomers acting as nano reactors during the polymerization process, which can be performed by the chemical or electrochemical oxidation. Furthermore, the molecules of the surfactant can help to disperse the monomer in the aqueous medium and not only act as a directing agent, but also can work as a dopant of the conducting polymer, enhancing the conductivity of the material. In turn, the synthesis of conducting polymer composites, such as CPHs, can be performed through different methods, highlighting: chemical or electro polymerization of the CP monomer in a pre-formed hydrogel matrix; or a mixture of the components of the hydrogel and the conducting polymer followed by simultaneous or gradual polymerization. The final product consists of a hydrogel network in which the CP chains are physically trapped in the hydrogel matrix [5].

Conclusion

Among the methods to produce the CPs, the electrochemical synthesis can be highlighted due to its simplicity, cost-effectiveness, reproducibility and allowing the fabrication of thin and uniforms materials. In these syntheses, generally, polymers are prepared by anodic oxidation of monomers, involving the generation of intermediate species, which must be stabilized to favor coupling reactions. As these intermediate species are positively charged, they are sensitive to nucleophilicity of the medium close to the electrode. Therefore, the solvent used in the synthesis must have a dielectric constant high enough to dissociate the electrolyte used, usually low nucleophilic anion derived from strong acids, be fluid (low viscosity) and remain liquid in a wide temperature range to facilitate ion transport in solution. Thus, as beforementioned, the reaction medium has a preponderant role in the process of synthesis of CPs. Therefore, the selection of the solvent must be accurate so that the final product, polymer or copolymer, has the desired characteristics, because it influences the ion diffusion, the morphology and the optoelectronic properties of the polymeric matrices.

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